REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
07-07-2016	Final Report	1-Aug-2015 - 30-Apr-2016

4. TITLE AND SUBTITLE
Final Report: Post-shock Sampling of Shock-heated Hydrocarbon Fuels

5a. CONTRACT NUMBER
W911NF-15-1-0434

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

6. AUTHORS
R. K. Hanson

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
Stanford University
3160 Porter Drive
Suite 100
Stanford, CA 94304 -8445

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
66415-EG-II.1

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
We have acquired a gas chromatograph (GC) to investigate post-shock sampling of shock-heated hydrocarbon fuels. The GC has four analytical columns, which allow for the precise measurement of permanent gases (e.g. O2, N2, CO, CO2, CH4), clear separation (and therefore measurement) of C2 and C3 hydrocarbons, and detection of aromatics and hydrocarbons C4 and larger. A sampling system has been implemented on one of our existing shock tube facilities and is used to extract a 13 cm3 sample of shock-heated gas, 2 cm from the shock tube end wall. GC analysis of the gas sample yields a measurement of the ultimate values of species at the end of the reflected shock

15. SUBJECT TERMS
Gas sampling, shock tube, jet fuel, gas chromatography

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Ronald Hanson
UU	UU	UU	UU		19b. TELEPHONE NUMBER 650-723-6850

Report Title

Final Report: Post-shock Sampling of Shock-heated Hydrocarbon Fuels

ABSTRACT

We have acquired a gas chromatograph (GC) to investigate post-shock sampling of shock-heated hydrocarbon fuels. The GC has four analytical columns, which allow for the precise measurement of permanent gases (e.g. O2, N2, CO, CO2, CH4), clear separation (and therefore measurement) of C2 and C3 hydrocarbons, and detection of aromatics and hydrocarbons C4 and larger. A sampling system has been implemented on one of our existing shock tube facilities and is used to extract a 13 cm3 sample of shock-heated gas, 2 cm from the shock tube end wall. GC analysis of the gas sample yields a measurement of the ultimate values of species at the end of the reflected shock test time. Simultaneous in-situ optical measurements allow for a direct comparison of the sampled and optically measured results. Initial experimental results show good agreement between optical measurements and GC analysis results.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received	Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Alison Ferris	0.20	
FTE Equivalent:	**0.20**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Ronald Hanson	0.02	Yes
FTE Equivalent:	**0.02**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
David Davidson	0.02
FTE Equivalent:	**0.02**
Total Number:	**1**

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment.

Technology Transfer

Discussions with Prof. Ken Brezinsky of UIC about GC sampling in shock tubes directed towards improvements in species measurement strategies.

Final Report

Post-shock Sampling of Shock-heated Hydrocarbon Fuels

by

R. K. Hanson
Mechanical Engineering Department
Stanford University, Stanford CA 94305

Short Term Innovative Research (STIR) Program
BAA W911NF-12-R-0012-02
Mechanical Sciences
Area 1.4 Propulsion and Energetics

Technical Point of Contact:
Dr. Ralph A. Anthenien
ralph.a.anthenien2.civ@mail.mil
919-549-4317

Submitted to:
Army Research Office
Engineering Sciences Directorate
Mechanical Sciences Research Program
Propulsion and Energetics Section
Dr. Ralph Anthenien Jr.

July 2016

Table of Contents

Abstract

We have acquired a gas chromatograph (GC) to investigate post-shock sampling of shock-heated hydrocarbon fuels. The GC has four analytical columns, which allow for the precise measurement of permanent gases (e.g. O_2, N_2, CO, CO_2, CH_4), clear separation (and therefore measurement) of C2 and C3 hydrocarbons, and detection of aromatics and hydrocarbons C4 and larger. A sampling system has been implemented on one of our existing shock tube facilities and is used to extract a 13 cm^3 sample of shock-heated gas, 2 cm from the shock tube end wall. GC analysis of the gas sample yields a measurement of the ultimate values of species at the end of the reflected shock test time. Simultaneous *in-situ* optical measurements allow for a direct comparison of the sampled and optically measured results. Initial experimental results show good agreement between optical measurements and GC analysis results.

Problem Statement

Stanford's recent work on a fast-kinetics scheme to model the pyrolysis reactions that dominate the first phase of hydrocarbon oxidation relies on the ability to measure key hydrocarbon fragments (e.g. ethylene, methane, and acetylene) over a wide range of temperatures and pressures. The optical diagnostics developed at Stanford for measuring the time-resolved formation of these key species are crucial to this endeavor, but the addition of an extractive, sampling-based measurement technique allows for the measurement of species not yet measureable by optical methods (e.g. H_2, benzene). Additionally, simultaneous laser- and sampling-based measurements provide the opportunity for a direct comparison of the two measurement techniques.

Gas Chromatograph (GC) Sampling System

We have acquired a 4-column GC (Agilent 490 MicroGC) for analysis of post-shock gas samples. Each of the four columns (MolSieve 5Å, PoraPLOT U, PoraPLOT Q, CP-Sil 5 CB) targets a specific kind of species or subset of hydrocarbons. A ¼-inch diameter sampling line is mounted on the Stanford Aerosol Shock Tube (AST) via a custom-made sidewall plug. The plug is located 2 cm from the shock tube end wall. A fast-acting valve is located between the sample line and the plug. A schematic of the sampling system is shown in Figure 1.

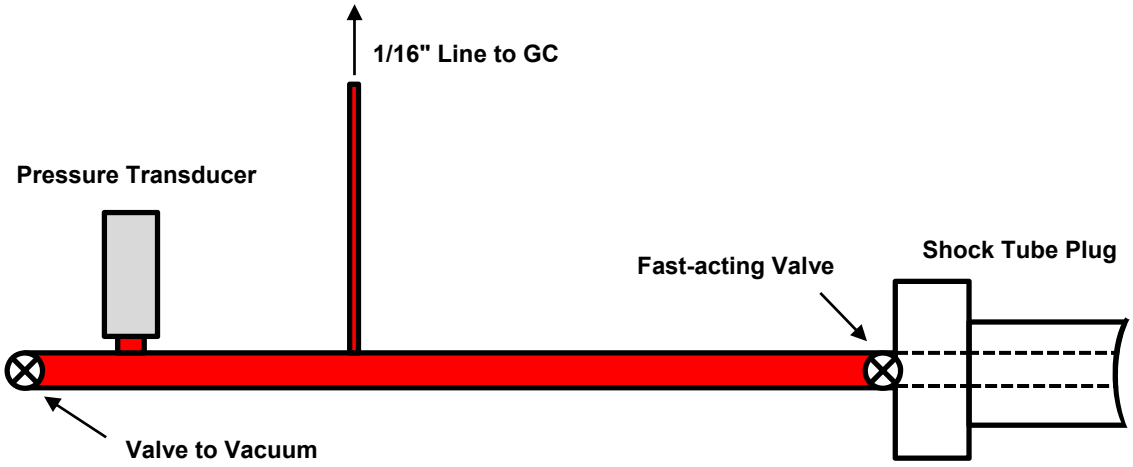

Figure 1: Schematic of GC sampling system

Before running a shock experiment, the fast-acting valve is closed and the sample line is evacuated. When a shock experiment is conducted, the vacuum valve is closed, thereby isolating the sample line. The sampling event is initiated when the fast-acting valve is triggered by the arrival of the reflected shock wave 2 cm from the end wall, and lasts for 1 sec.

Results Summary

A series of experiments was conducted to validate the sampling system results and explore the thermal decomposition of ethylene and methane. Initially, a 1% ethylene/0.1% methane/balance argon fuel mixture was shock-heated to ~960 K – a temperature low enough that no reaction would occur. GC analysis of the post-shock gas sample showed an average of 100.0% and 100.2% recovery of the ethylene and methane, respectively. A CO_2 gas laser (10.532 micron emission line) was used to simultaneously record time-resolved ethylene mole fraction. Like the GC measurements, the optical measurements showed 98% ethylene retention between initial fuel loading and post-shock conditions.

In-situ optical and sampled-gas results were recorded for the same fuel mixture (1% ethylene/0.1% methane/argon) over a range of temperatures (1200-1900 K) at ~4.5 atm. The GC was used to measure the ultimate values of four species (ethylene, methane, acetylene, and hydrogen) at each shock condition. The CO_2 gas laser was used to measure ethylene mole fraction as a function of time, and the ultimate value for each shock condition was taken to be the ethylene mole fraction when the test pressure drops to 80% of the constant P5 value. Additionally, the two experimental values were compared to results modeled using the USC Mech Version II chemical kinetic mechanism (Wang et al.)[1]. Figure 2 shows a comparison of the three ethylene data points for each shock condition.

[1] Hai Wang, Xiaoqing You, Ameya V. Joshi, Scott G. Davis, Alexander Laskin, Fokion Egolfopoulos & Chung K. Law, USC Mech Version II. High-Temperature Combustion Reaction Model of H2/CO/C1-C4 Compounds. http://ignis.usc.edu/USC_Mech_II.htm, May 2007.

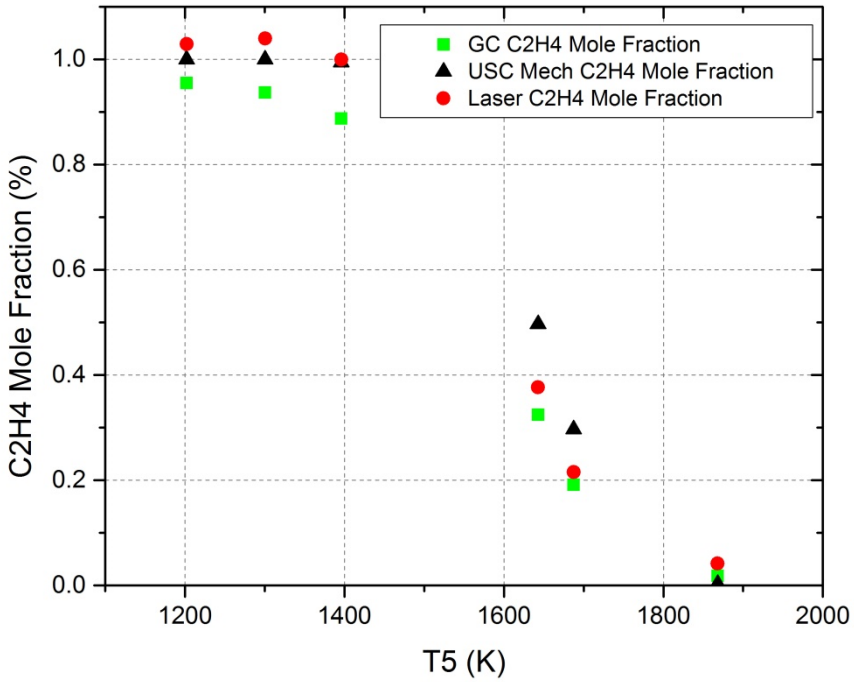

Figure 2: Ultimate ethylene mole fraction values (comparison of GC, laser, and USC Mech version II results)

Figures 3-5 show the three additional species (methane, acetylene, and hydrogen) measured using the GC that were not measured optically. The results are again compared to results modeled using the USC Mech Version II mechanism.

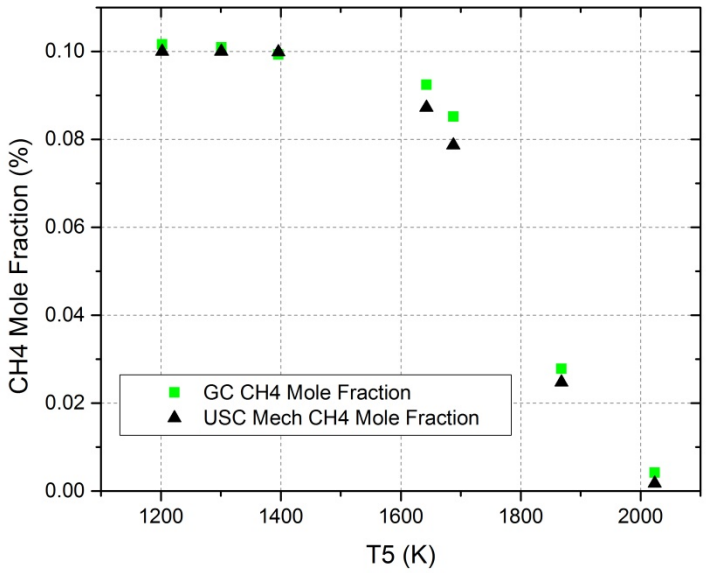

Figure 3: Ultimate methane mole fraction values (comparison of GC and USC Mech version II results)

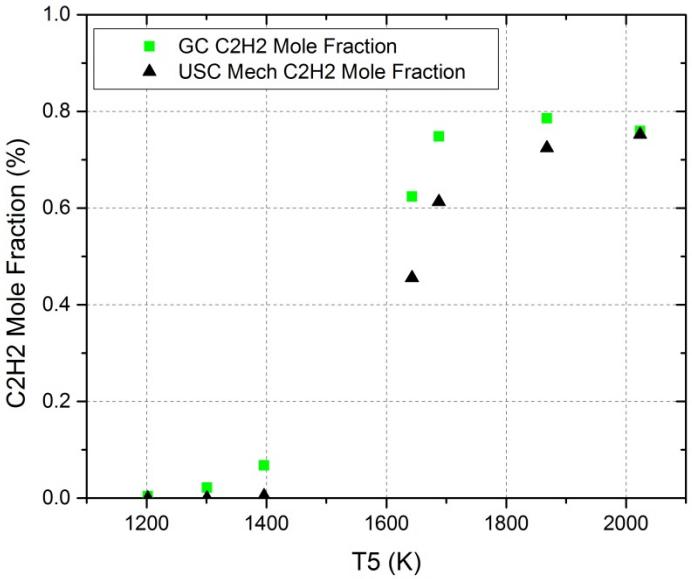

Figure 4: Ultimate acetylene mole fraction values (comparison of GC and USC Mech version II results)

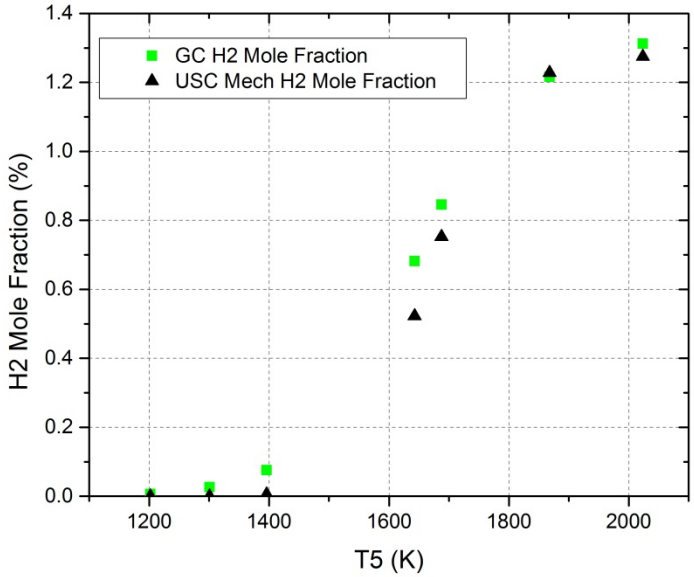

Figure 5: Ultimate H2 mole fraction values (comparison of GC and USC Mech version II results)

As indicated above, the GC measurements capture the temperature-dependent trends expected from the pyrolysis of a 1% ethylene/0.1% methane fuel mixture. The GC methane measurements in particular show close agreement with the kinetic mechanism results. Larger discrepancies between GC measurements, optical measurements, and mechanism results (e.g. Figure 1) indicate that further work is necessary to optimize the sampling process and improve the accuracy of the GC analysis.

Future Work

The initial GC measurements taken using the newly implemented post-shock sampling system are quite promising – temperature-dependent trends can be captured by analyzing post-shock gas

samples and relatively good agreement can be seen between GC, laser, and modeled mechanism results. A number of procedural and structural changes to the sampling system have been identified and will be implemented to improve the fidelity of the GC analysis results. The improved sampling system will then be used to explore larger, single-component hydrocarbon fuels (e.g. n-heptane, n-dodecane), followed by real fuels, including JP-8 and diesel. The suite of species analyzed using the GC will be expanded and additional optical diagnostics will be implemented for comparison.